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[54] MICROWAVE DIELECTRIC CERAMIC COMPOSITION

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Nov. 19, 1991	[JP]	Japan	3-303293
Dec. 6, 1991	[JP]	Japan	3-323237

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[52] **U.S. Cl.** **501/136**; 501/134; 501/135; 252/62.9; 252/518; 252/520; 252/521; 423/592; 423/593; 423/598; 423/641

[58] **Field of Search** 501/134, 135, 136, 139, 501/137; 252/518, 519, 520, 521, 62.9; 423/592, 593, 598, 641

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Assistant Examiner—Michael Marcheschi
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[57] **ABSTRACT**

A microwave dielectric ceramic composition which is obtained by selecting, in a composition formula of $(A^{1+}{}_{\frac{1}{2}} \cdot B^{3+}{}_{\frac{1}{2}})\ TiO_3$, Li^{1+} and Nd^{3+}, Co^{3+} or Pr^{3+} as A^{1+} and B^{3+}, respectively. The dielectric ceramic composition expressed by $(A^{1+}{}_{\frac{1}{2}} \cdot B^{3+}{}_{\frac{1}{2}})\ TiO_3$ has a high dielectric constant and has a temperature coefficient of resonance frequency τf which is large on the minus side. MgO, CoO, ZnO, $CaCO_3$ or $SrCO_3$ is added to such a dielectric ceramic composition expressed by $(A^{1}+{}_{\frac{1}{2}} \cdot B^{3}+{}_{\frac{1}{2}}/TiO_3$, to improve the Q value of the dielectric ceramic composition.

15 Claims, 3 Drawing Sheets

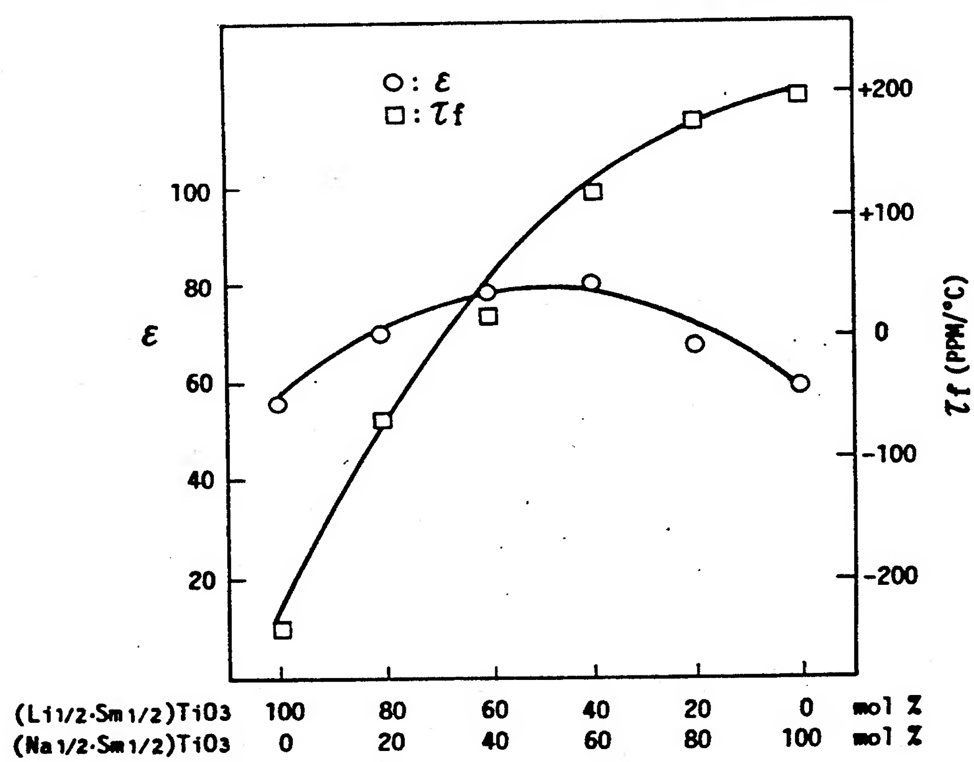
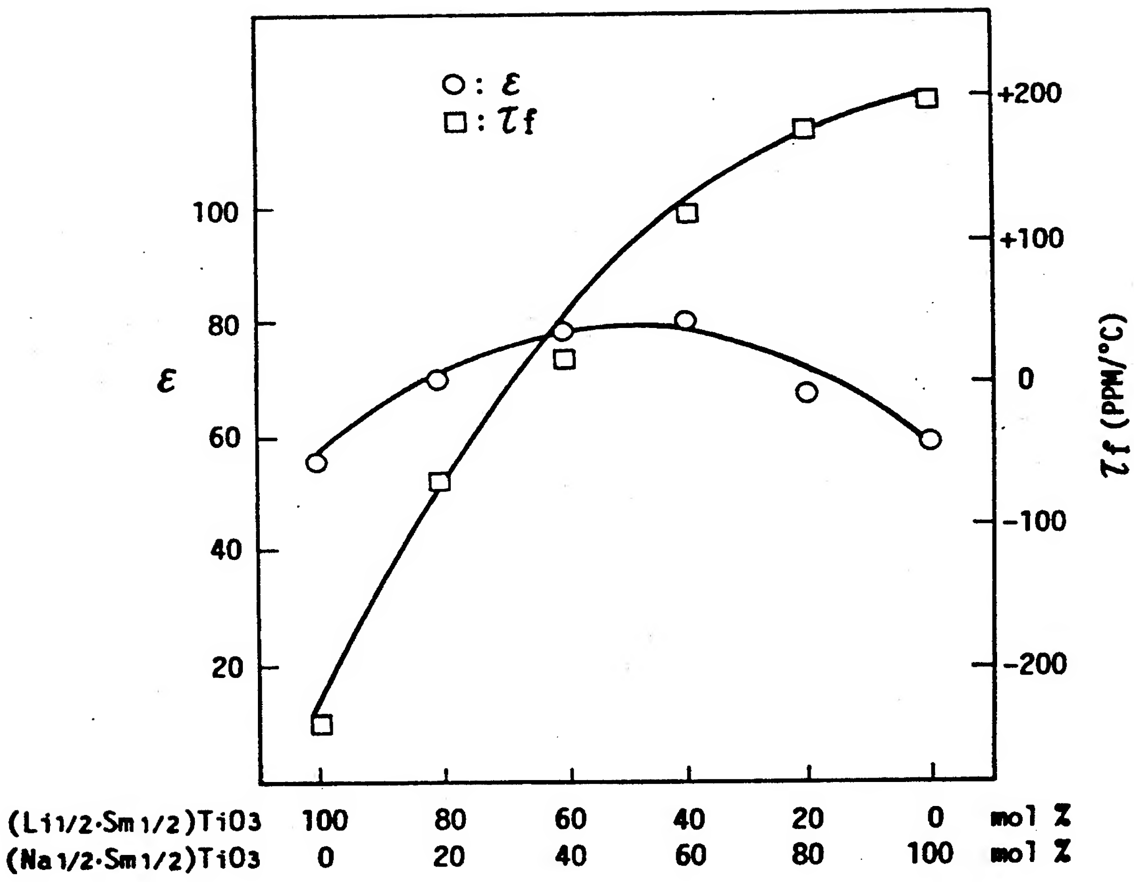


Fig. 1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□ : τf
100
80
ε
60
40
20
+200
+100
0
−100
−200
τf (PPM/°C)
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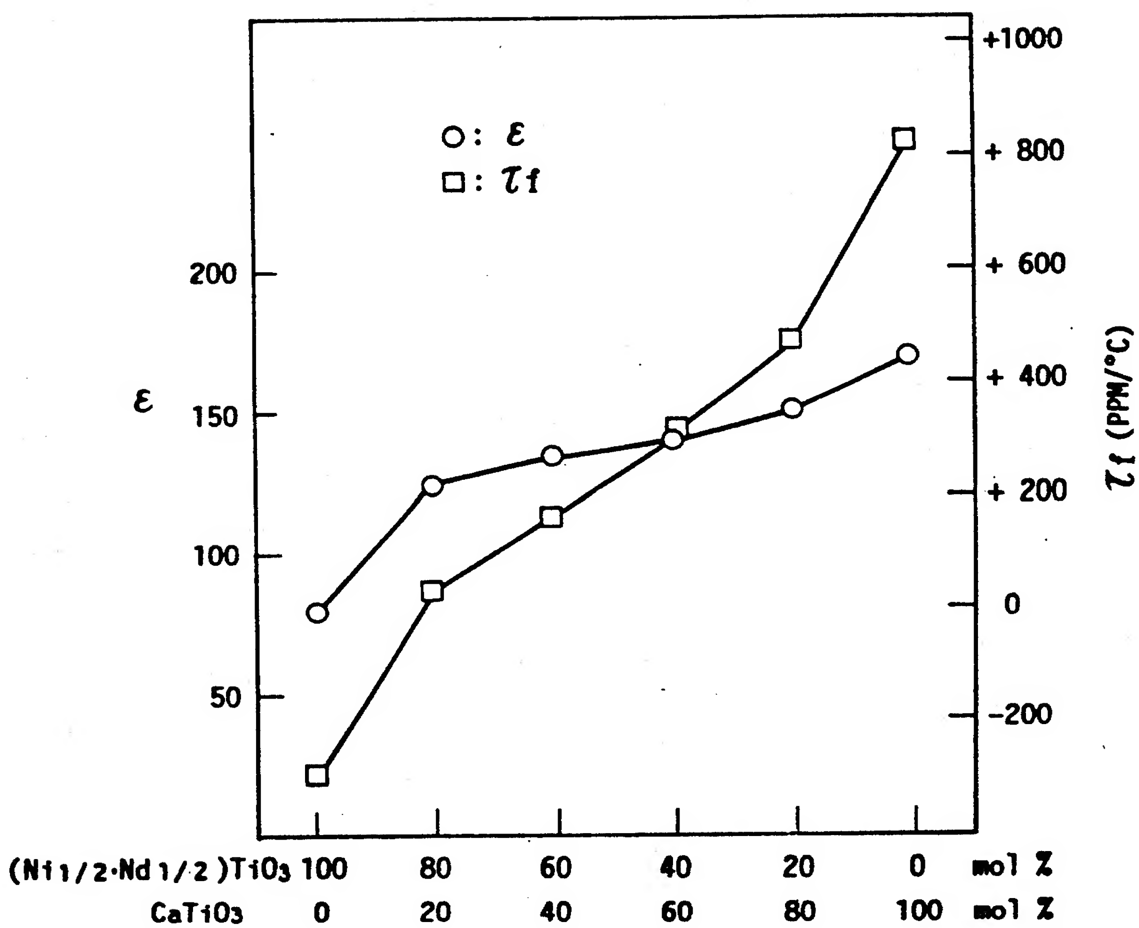
(Na1/2·Sm1/2)TiO3 0 20 40 60 80 100 mol %

Fig. 2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100
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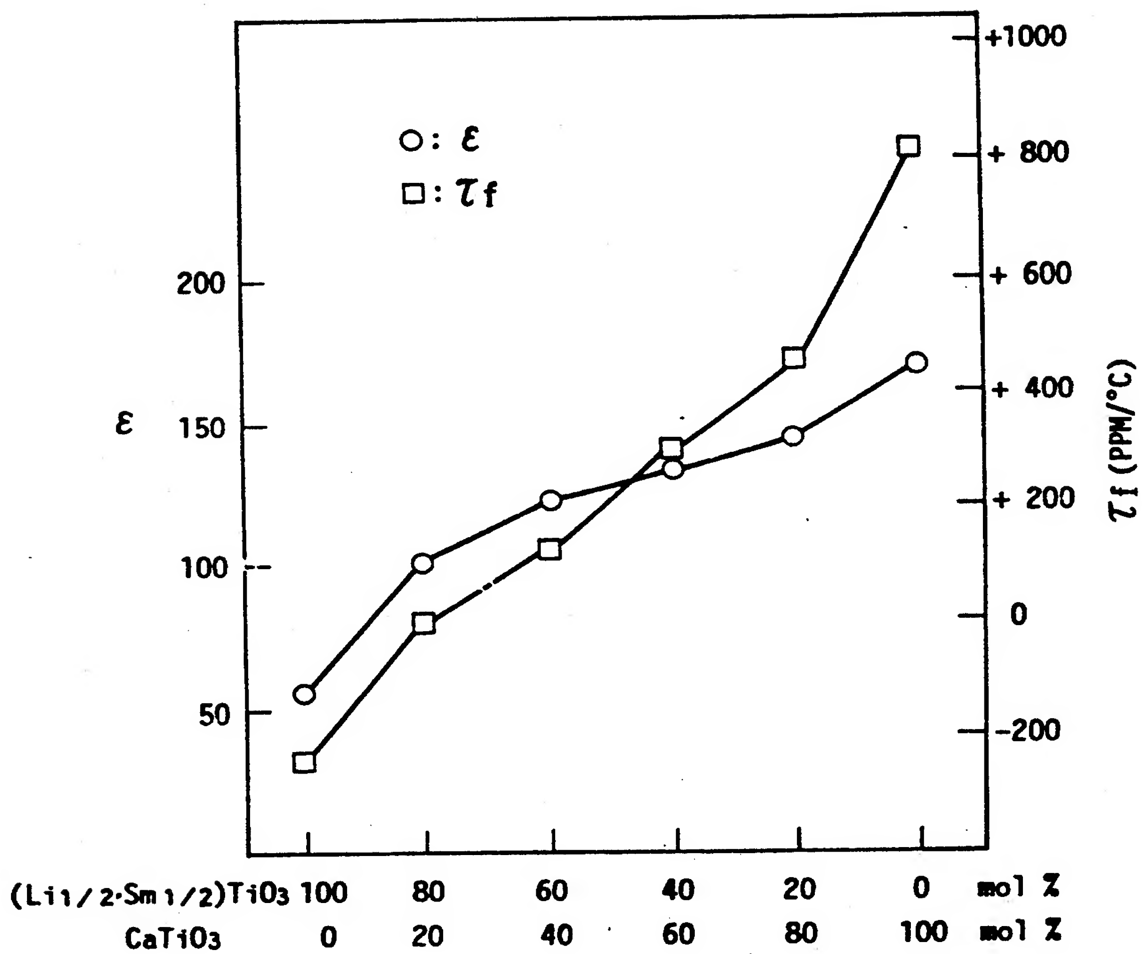
+ 600
+ 400
+ 200
0
−200
τf (PPM/°C)
$(Ni_{1/2} \cdot Nd_{1/2})TiO_3$ 100 80 60 40 20 0 mol %
$CaTiO_3$ 0 20 40 60 80 100 mol %

Fig. 3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150
100
50
ε
+1000
+ 800
+ 600
+ 400
+ 200
0
−200
τf (PPM/°C)
(Li1/2·Sm1/2)TiO3 100 80 60 40 20 0 mol %
CaTiO3 0 20 40 60 80 100 mol %

MICROWAVE DIELECTRIC CERAMIC COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to dielectric ceramic compositions for use as resonators employed in a microwave frequency band of several gigahertz.

2. Description of the Prior Art

In recent years, attempts have been made to use a dielectric material for a resonator or a filter used in satellite communication, broadcasting and microwave remote communication using a microwave a frequency band of several gigahertz. A transmitter-receiver such as a microwave remote recognition system is also sought.

Examples of this type of dielectric ceramic material conventionally used include a composition of a BaO-TiO_2-Nd_2O_3-Bi_2O_3 system which is proposed in, for example, Japanese Patent Laid-Open Gazette No. 8806/1986. In this conventional dielectric ceramic composition, its dielectric constant ϵ is as high as 70 to 90. In addition, the temperature coefficient of resonance frequency τf of the dielectric ceramic composition is also high, i.e., +10 to about +20 PPM/°C., so that sufficient properties cannot be obtained.

Meanwhile, when a dielectric resonator is constructed, the higher the dielectric constant ϵ of a material used, the smaller the size the resonator can be. Accordingly, a material having a higher dielectric constant ϵ is desired.

Examples of a material having a high dielectric constant ϵ include $SrTiO_3$ and $CaTiO_3$. However, these cannot be used because the dielectric constant ϵ is very high, i.e., 300 and 180, while their temperature coefficient of resonance frequency τf is very high, i.e., +1700 PPM/°C. and +800 PPM/°C.

Examples of a method of reducing the temperature coefficient of resonance frequency τf of such a dielectric ceramic composition include a method of combining a material having a dielectric constant ϵ which is as high as possible and a temperature coefficient of resonance frequency τf which takes a minus value with the dielectric ceramic composition. According to this method, a ceramic composition having a high dielectric constant ϵ and having a low temperature coefficient of resonance frequency τf is obtained by a suitable combination.

In general, however, as the dielectric constant ϵ becomes higher, the temperature coefficient of resonance frequency τf becomes larger on the plus side. A material having a high dielectric constant ϵ and a temperature coefficient of resonance frequency τf which is large on the minus side has not been known.

SUMMARY OF THE INVENTION

The present invention has been made in view of the above described points and has for its object to obtain a dielectric ceramic composition having a high dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the minus side.

Another object of the present invention is to improve the Q value of such a dielectric ceramic composition.

Still another object of the present invention is to provide a dielectric ceramic composition having a high dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is close to zero.

When a microwave dielectric ceramic composition according to the present invention is expressed by a composition formula of $(A^{1+}{}_{1/2}\cdot B^{3+}{}_{1/2})\ TiO_3$, Li^{1+} and Nd^{3+}, Sm^{3+}, Co^{3+} or Pr^{3+} are respectively selected as A^{1+} and B^{3+}.

Furthermore, the present invention provides a dielectric ceramic composition obtained by suitably selecting MgO, CoO, ZnO, $CaCO_3$ or $SrCO_3$ and adding the same to the ceramic composition expressed by $(A^{1+}{}_{1/2}\cdot B^{3+}{}_{1/2})\ TiO_3$.

The above described dielectric ceramic composition expressed by $(A^{1+}{}_{1/2}\cdot B^{3+}{}_{1/2})\ TiO_3$ has a high dielectric constant ϵ and has a temperature coefficient of resonance frequency τf which is large on the minus side. MgO, CoO, ZnO, $CaCO_3$ or $SrCO_3$ is added to such a dielectric ceramic composition $(Li_{1/2}\cdot B^{3+}{}_{1/2})\ TiO_3$, thereby to improve the Q value of the dielectric ceramic composition.

Additionally, when the microwave dielectric ceramic composition according to the present invention is expressed by a composition formula of $w\cdot A^{1+}{}_2O - x\cdot A^{1+\prime}{}_2O - y\cdot B^{3+}{}_2O_3 - z\cdot TiO_2$ (where $w+x+y+z=100$ mole %), Li^{1+}, Na^{1+}, and Nd^{3+} or Sm^{3+} are respectively selected as A^{1+}, $A^{1+\prime}$, and B^{3+}.

As described in the foregoing, a dielectric ceramic composition mainly composed of Li_2O-Na_2O-Sm_2O_3-TiO_2 and a dielectric ceramic composition mainly composed of Li_2O-$Na_{Na2}O$-Nd_2O_3-TiO_2 have a high dielectric constant ϵ and have a low temperature coefficient of resonance frequency τf.

Furthermore, when the microwave dielectric ceramic composition according to the present invention is expressed by a composition formula of $v\cdot B^{3+\prime}{}_2O_3 - w\cdot A^{1+}{}_2O - x\cdot A^{1+\prime}{}_2O - y\cdot B^{3+}{}_2O_3 - z\cdot TiO_2$ (where $v+w+x+y+z=100$ mole %), Li^{1+}, Na^{1+}, Sm^{3+}, and Nd^{3+} or Pr^{3+} are respectively selected as A^{1+}, $A^{1+\prime}$, B^{3+}, and $B^{3+\prime}$.

As described in the foregoing, a dielectric ceramic composition mainly composed of Nd_2O_3-Li_2O-Na_2O-Sm_2O_3-TiO_2 and a dielectric ceramic composition mainly composed of Pr_2O_3-Li_2O-Na_2O-Sm_2O_3-TiO_2 have a high dielectric constant ϵ and have a low temperature coefficient of resonance frequency τf.

Furthermore, when the microwave dielectric ceramic composition according to the present invention is expressed by a composition formula of $w\cdot A^{1+}{}_2O - x\cdot CaO - y\cdot B^{3+}{}_2O_3 - z\cdot TiOhd\ 2$ (where $w+x+y+z=100$ mole %), Li^{1+} and Sm^{3+} or Nd^{3+} are respectively selected as A^{1+} and B^{3+}. Thus, a dielectric ceramic composition mainly composed of Li_2O-CaO-Sm_2O_3-TiO_2 and a dielectric ceramic composition mainly composed of Li_2O-CaO-Nd_2O_3-TiO_2 have a high dielectric constant ϵ and have a low temperature coefficient of resonance frequency τf.

Additionally, when the microwave dielectric ceramic composition according to the present invention is expressed by a composition formula of $x\cdot(Li_{1/2}\cdot B^{3+}{}_{1/2})\ TiO_3 - (100-x)\cdot CaTiO_3$ (Where 0 mole % $<x<$ 100 mole %), Nd^{3+} or Sm^{3+} is selected as B^{3+}.

Furthermore, when the microwave dielectric ceramic composition according to the present invention is expressed by a composition formula of $x\cdot(Li_{1/2}\cdot B^{3+}{}_{1/2})\ TiO_3 - 100 - x)\cdot(Na_{1/2}\cdot C^{3+}{}_{1/2})\ TiO_3$ (where 0 mole % $<x<$ 100 mole %), Nd^{3+} or Sm^{3+} and Nd^{3+} or Sm^{3+} are respectively selected as B^{3+} and C^{3+}.

Moreover, the above described dielectric ceramic composition $(Li_{1/2}\cdot B^{3+}_{1/2})\,TiO_3$ and a dielectric ceramic composition $(Na_{1/2}\cdot C^{3+}_{1/2})\,TiO_3$ or $CaTiO_3$ are combined with each other, thereby to obtain a dielectric ceramic material having a high dielectric constant ϵ and having a low temperature coefficient of resonance frequency τf.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a characteristic diagram showing a characteristic curve of a dielectric constant ϵ and a temperature coefficient of resonance frequency τf against the mixture ratio of $(Li_{1/2}\cdot Sm_{1/2})\,TiO_3$ to $(Na_{1/2}\cdot Sm_{1/2})\,TiO_3$ according to the present invention;

FIG. 2 is a characteristic diagram showing a characteristic curve of a dielectric constant ϵ and a temperature coefficient of resonance frequency τf against the mixture ratio of $(Li_{1/2}\cdot Nd_{1/2})\,TiO_3$ to $CaTiO_3$ according present invention; and

FIG. 3 is a characteristic diagram showing a characteristic curve of a dielectric constant ϵ and a temperature coefficient of resonance frequency τf against the mixture ratio of $(Li_{1/2}\cdot Sm_{1/2})\,TiO_3$ to $CaTiO_3$ according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Description is now made of a first embodiment of the present invention.

A microwave ceramic composition according to the first embodiment is obtained by selecting, in a composition formula of $(A^{1+}_{1/2}\cdot B^{3+}_{1/2})\,TiO_3$, Li^{1+} and Nd^{3+}, Sm^{3+}, Co^{3+} or Pr^{3+} as A^{1+} and B^{3+}, respectively.

First, a method of fabricating the microwave ceramic composition will be described.

As raw materials, high-purity powders of TiO_2, Li_2CO_3, Nd_2O_3, Sm_2O_3, Co_2O_3, Pr_6O_{11} were weighed so as to be predetermined molar fractions. For example, used as TiO_2 is one of a high-purity grade which is manufactured by Toho Titanium Co., Ltd.; used as Li_2CO_3 is one of a 3N grade which is manufactured by Kojundo Kagaku Co., Ltd.; used as Nd_2O_3 is one of a 3N grade which is manufactured by Mitui Mining and Smelting Co., Ltd.; used as Co_2O_3 is one of a reagent grade which is manufactured by Kojundo Kagaku Co., Ltd.; and used as Pr_6O_{11} is one of a 3N grade which is manufactured by Mitui Mining and Smelting Co., Ltd.

Description is made of a specific example of the fabrication of the microwave dielectric ceramic composition according to the present embodiment using the above described raw materials.

First, as molar fractions of the high-purity powders of TiO_2, Li_2CO_3, Nd_2O_3, Sm_2O_3, Co_2O_3, and Pr_6O_{11}, TiO_2 shall be 1 mole, Li_2CO_3 shall be ¼ mole, Nd_2O_3 shall be ¼ mole when Nd_2O_3 is selected in addition thereto, Sm_2O_3 shall be ¼ mole when Sm_2O_3 is selected in addition thereto, Co_2O_3 shall be ¼ mole when Co_2O_3 is selected in addition thereto, and Pr_6O_{11} shall be 1/12 mole when Pr_6O_{11} is selected in addition thereto.

The raw material powders, a nylon ball of 15ϕ and ethyl alcohol were put in a nylon pot, mixed in the following condition, and wet-blended for eight hours.

Raw material powders:Nylon ball:Ethyl alcohol=100 g:500 g:500 cc

The blended powder was then dried at 120° C. for 24 hours. The dried powder was crushed in a mortar made of alumina. The crushed powder was packed in a boat made of magnesia (MgO) and calcined at 900° to 1200° C., and particularly, at 1150° C. in the present embodiment for two hours. The calcined powder is crushed again in the mortar.

This crushed powder was put in the nylon pot under the following condition and wet-ground for 20 to 60 hours, and particularly, for 30 hours, in the present embodiment.

Crushed powder:Nylon ball:Ethyl alcohol=100 g:1000 g:500 cc

Subsequently, this ground powder was dried at 120° C. for 24 hours. The dried ground powder was crushed, and a 10 solution of polyvinyl alcohol is mixed as a binder so as to account for three per cent of 50 g of the powder using the mortar to granulate the powder. The granulated powder was dried at 100° C. for five hours.

Thereafter, the dried powder was classified using two types of screens, that is, a 100-mesh screen (150 μm) and a 200-mesh screen (75 μm), to take out only grains having a diameter of 75 to 150 μm.

The classified powder was pressed into a disc having a diameter of 10 mm and a thickness of 6 mm at a pressure of 2000 to 3000 Kg/cm^2, and particularly, 2550 Kg/cm^2, in the present embodiment.

Subsequently, the pressed forming powder was put in a boat for sintering made of alumina with a plate made of zirconia (ZrO_2) being laid on the bottom thereof, and was held and sintered for two hours at 350° C., for two hours at 600° C. and for five hours at 1300° C. at a heating rate of 150° C./H. Both surfaces of the sintered object ware polished using abrasive powder OF-800# manufactured by, for example, Fujimi Abrasive Co., Ltd. such that the thickness of the sintered object is one-half of the diameter thereof. In addition, both surfaces of the polished object were polished clean again using wet abrasive paper 1500#. Thereafter, the polished object was ultrasonic cleaned by acetone and finally, dried at 100° C. for two hours to prepare a sample.

The dielectric constant ϵ and the Q value of the sample thus prepared were measured using a network analyzer (YHP 8510B) in the neighborhood of the measurement frequency of 3 GHz using the dielectric resonator method (Hakki-Coleman method). In addition, the temperature coefficient of resonance frequency τf was calculated from the following equation by putting a measuring system in a constant temperature bath to measure the change in resonance frequency at 0° to 70° C.:

$$f = \frac{F_{70} - F_{20}}{F_{20} \times \Delta T} \times 10^6 (\mathrm{PPM/^\circ C.})$$

where F_{70} denotes a resonance frequency at 70° C., F_{20} denotes a resonance frequency at 20° C., and ΔT denotes a temperature difference.

The results of measurements made by varying A^{1+} and B^{3+} are shown in Table 1.

TABLE 1

sample number	composition A^{+1}	composition B^{3+}	dielectric properties: dielectric constant ϵ	dielectric properties: Q value	dielectric properties: τf (PPM/°C.)	note
1	Li^{1+}	Nd^{3+}	80	430	−310	
2	Li^{1+}	Sm^{3+}	52	470	−260	

TABLE 1-continued

number	sample composition A^{+1}	sample composition B^{3+}	dielectric properties: dielectric constant ε	dielectric properties: Q value	dielectric properties: τf (PPM/°C.)	note
3	Li^{1+}	Co^{3+}	31	2200	−58	
4	Li^{1+}	Pr^{3+}	92	340	−405	
5*	Li^{1+}	Cr^{3+}	—	—	—	impossible to measure
6*	Li^{1+}	La^{3+}	—	—	—	impossible to measure
7*	K^{1+}	Nd^{3+}	—	—	—	impossible to measure

In the table 1, asterisked samples 5 to 7 are comparative examples beyond the scope of the present invention. In a combination in the comparative example, the sample is sintered. However, the sample is inferior in dielectric properties in the microwave region, thereby making it impossible to measure the sample.

On the other hand, as can be seen from the table 1, a ceramic composition having a high dielectric constant ε and having a temperature coefficient of resonance frequency τf which is large on the minus side is obtained by selecting, in a composition formula of $(A^{1+}{}_{1/2}\cdot B^{3+}{}_{1/2})$ TiO_3, TiO_3, Li^{1+} and Nd^{3+}, Sm^{3+}, Co^{3+} or Pr^{3+} as A^{1+} and B^{3+}, respectively.

Description is now made of a second embodiment. A ceramic composition according to the second embodiment is obtained by adding to the ceramic composition $(Li_{1/2}\cdot B^{3+}{}_{1/2})$ TiO_3 obtained in the above described first embodiment MgO, CoO or ZnO when B^{3+} is Nd^{3+} or Pr^{3+} or $CaCO_3$, $SrCO_3$ or ZnO when B^{3+} is Sm^{3+}. A predetermined part by weight of $CaCO_3$. $SrCO_3$ or ZnO is added to 100 parts by weight of main components of $(Li_{1/2}\cdot B^{3+}{}_{1/2})$ TiO_3. As this additive, used as $CaCO_3$ is one of a reagent grade which is manufactured by Kishida Chemical Co., Ltd., used as $SrCO_3$ is one of a reagent grade which is manufactured by Kishida Chemical Co., Ltd., or used as ZnO is one of a 3N grade which is manufactured by Kojundo Kagaku Co., Ltd.

In the second embodiment, a predetermined amount of the above described additive is mixed with powder obtained by wet-blending respective raw materials of the main components of $(Li_{1/2}\cdot B^{3+}{}_{1/2})$ TiO_3, followed by dryblending. Thereafter, a sample is completed by calcination, forming and sintering in the same method as that in the first embodiment.

The results of measurements made of the dielectric properties of samples to be measured which are prepared by varying the amount of addition of each of the above described additives in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 2, Table 3 and Table 4.

Table 2 shows the results of measurements made when MgO, CoO or ZnO is added to $(Li_{1/2}\cdot Nd^{3+}{}_{1/2})$ TiO_3.

Table 3 shows the results of measurements made when $CaCO_3$, $SrCO_3$ or ZnO is added to $(Li_{1/2}\cdot Sm^{3+}{}_{1/2})$ TiO_3.

Table 4 shows the results of measurements made when MgO, CoO or ZnO is added to $(Li_{1/2}\cdot Pr^{3+}{}_{1/2})$ TiO_3.

TABLE 2

sample number	additive (part by weight)	dielectric properties: dielectric constant ε	dielectric properties: Q value	dielectric properties: τf (PPM/°C.)
	MgO			
8	0	80	430	−310
9	1	71	900	−207
10	3	56	1873	−149
11	5	48	1939	−150
12	10	40	2023	−194
	CoO			
13	0	80	430	−310
14	1	71	844	−262
15	3	64	1318	−173
16	5	57	1936	−145
17	10	44	3181	−82
	ZnO			
18	0	80	430	−310
19	1	71	841	−275
20	3	66	1183	−169
21	5	55	2203	−126
22	10	42	2841	−27

TABLE 3

sample number	additive (part by weight)	dielectric properties: dielectric constant ε	dielectric properties: Q value	dielectric properties: τf (PPM/°C.)
	$CaCo_3$			
23	0	52	470	−260
24	1	56	676	−322
25	3	62	1301	−154
26	10	49	1073	−275
27*	15	58	1680	−38
	$SrCO_3$			
28	0	52	470	−260
29	3	60	833	−272
30	5	63	909	−267
31	10	55	916	−232
32*	15	65	386	−45
	ZnO			
33	0	52	470	−260
34	1	59	752	−230
35	3	48	1003	−192
36	5	43	767	−110
37*	15	35	1196	57

TABLE 4

sample number	additive (part by weight)	dielectric properties: dielectric constant ε	dielectric properties: Q value	dielectric properties: τf (PPM/°C.)
	MgO			
38	0	92	340	−405
39	1	71	632	−307
40	3	61	806	−210
41	10	43	941	−173
42*	20	27	1057	−67
	CoO			
32	0	92	340	−405
44	3	67	714	−258
45	5	75	555	−336
46	10	46	1518	−96
47*	20	32	4111	+32
	ZnO			
48	0	92	340	−405
49	1	76	539	−360
50	3	67	732	−276
51	5	57	1097	−100
52*	20	32	6355	20

In the tables, asterisked samples 27, 32, 37, 42, 47 and 52 are comparative examples beyond the scope of the present invention.

As can be seen from the tables 2 to 4, the Q value is improved by the addition of each of the additives. However, as the amount of the addition is increased, the Q value becomes larger, while the dielectric constant become lower. Consequently, the amount of the addition of each of the additives is suitably not more than 10 parts by weight per 100 parts by weight of $(Li_{\frac{1}{2}} \cdot B^{3+}_{\frac{1}{2}})TiO_3$.

Description is now made of a third embodiment.

A microwave ceramic composition according to the third embodiment is obtained by selecting, in a composition formula of $(A^{1+} \cdot A^{1+'})_2O\text{-}B^{3+}{}_2O_3\text{-}TiO_2$, Li^{1+}, Na^{1+}, and Nd^{3+} as A^{1+}, $A^{1+'}$, and B^{3+}, respectively. In the third embodiment, to prepare samples high-purity powders of TiO_2, Li_2CO_3, Na_2CO_3, and Nd_2O_3 are used as raw materials, and the mixture ratio of the respective raw materials is changed in the same method as that in the first embodiment. The dielectric properties of the samples measured in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 5. In the table, w, x, y and z indicate molar fractions, where $w+x+y+z=100$ mole %.

TABLE 5

sample number	composition ratio (mole %) w.Li₂O—x.Na₂O—y.Nd₂O₃—z.TiO₂ w	x	y	z	dielectric properties ε	Q value	τ f(PPM/°C.)
53	1.00	8.33	18.13	72.54	76	805	+70
54	1.50	8.33	18.03	72.14	97	715	+57
55	2.00	8.33	17.93	71.74	96	665	+52
56	2.50	8.33	17.83	71.34	103	710	+41
57	3.00	8.33	17.73	70.94	104	720	+35
58	4.00	8.33	17.53	70.14	106	654	+21
59	4.36	4.55	18.22	72.87	98	810	−15
60	5.00	8.33	17.33	69.34	109	569	−2
61	5.82	4.55	17.93	71.70	101	740	−55
62	7.00	8.33	16.93	67.74	101	470	−80
63*	7.27	4.55	17.64	70.54	96	665	−83
64	9.00	8.33	16.93	67.74	101	470	−80
65	10.18	4.55	17.05	68.22	91	555	−255
66	13.09	4.55	16.47	65.89	93	325	−165

As can be seen from table 5, a dielectric ceramic composition expressed by a composition formula of $w \cdot Li_2O - x \cdot Na_2O - y \cdot Nd_2O_3 - z \cdot TiO_2$ ($w+x+y+z=100$ mole %) has a high dielectric constant ϵ, has a low temperature coefficient of resonance frequency τf and has a high Q value.

0.0 mole % $< w \leqq$ 17.0 mole %
0.0 mole % $\leqq x \leqq$ 17.0 mole %
0.0 mole % $< y \leqq$ 25.0 mole %
0.0 mole % $< z \leqq$ 80.0 mole %

Particularly when w, x, y and z are set in the following ranges, good dielectric properties are obtained:

3.0 mole % $\leqq w \leqq$ 15.0 mole %
3.0 mole % $\leqq x \leqq$ 15.0 mole %
9.0 mole % $\leqq y \leqq$ 25.0 mole %
0.0 mole % $\leqq z \leqq$ 80.0 mole %

Description is now made of a fifth embodiment.

A microwave ceramic composition according to the fifth embodiment is obtained by selecting, in a composition formula of $(A^{1+} \cdot A^{1+'})_2O - B^{3+}{}_2O_3 - TiO_2$, Li^{1+}, Na^{1+}, and Sm^{3+} as A^{1+}, $A^{1+'}$, and B^{3+}, respectively. In the fourth embodiment, high-purity powders of TiO_2, Li_2CO_3, Na_2CO_3, and Sm_2O_3 are used as raw materials, and the mixture ratio of the respective raw materials is changed in the same method as that in the first embodiment, to prepare samples. The dielectric properties of the samples measured in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 6. In the table, w, x, y and z indicate molar fractions, where $w+x+y+z=100$ mole %.

TABLE 6

sample number	composition ratio (mole %) w	x	y	z	dielectric properties ε	Q value	τ f(PPM/°C.)
	w.Li₂O—x.Na₂O—y.Nd₂O₃—z.TiO₂						
*67	0.00	16.67	16.67	66.66	73	2390	+213
68	3.00	6.68	18.67	71.66	80	1200	+51
69	3.60	6.68	17.96	71.76	80	1990	+41
70	3.75	6.68	17.17	72.41	83	2210	+44
71	4.50	6.68	18.67	70.16	80	2670	0
72	4.50	6.68	17.17	71.77	84	2100	+35
73	4.80	6.68	17.72	70.80	82	1870	+21
74	5.52	15.00	17.00	62.48	82	1790	+137
75	5.85	10.00	18.00	66.15	68	1610	+45
76	6.00	6.68	18.67	68.66	80	2530	−29
77	6.00	6.68	16.42	70.91	86	1590	+7
78	6.00	6.68	17.48	69.84	83	1975	+5
79	6.18	5.00	17.81	71.01	79	2750	−46
80	6.40	3.34	18.06	72.20	72	1180	−62
81	6.75	6.68	16.42	70.16	89	1180	−8
82	6.75	6.68	17.92	68.66	82	2140	−40
83	6.80	15.00	17.00	61.20	79	2270	+129
84	7.20	6.68	17.24	68.88	87	1430	−28
85	7.20	10.00	18.00	61.80	79	2140	+30

TABLE 6-continued

sample number	composition ratio (mole %) w	x	y	z	dielectric properties ε	Q value	τ f(PPM/°C.)
	$w.Li_2O—x.Na_2O—y.Nd_2O_3—z.TiO_2$						
86	7.76	3.00	19.40	69.84	71	1070	−119
87	8.00	3.34	16.33	72.33	74	2040	+8
88	8.00	3.34	17.74	70.92	72	2220	−91
89	8.00	3.34	19.33	69.33	71	2740	−122
90	8.10	10.00	17.10	64.80	85	1930	+44
91	8.75	3.00	18.74	69.74	72	2730	−132
92	9.00	3.34	18.33	69.33	70	2500	+138
93	10.80	6.68	16.52	66.00	102	1170	+55
94	12.00	6.68	16.28	65.04	82	1550	−20
95	14.40	3.34	16.46	65.80	68	1310	−184

In the table, an esterified sample 67 is a comparative example beyond the scope of the present invention.

As can be seen from the table 6, a dielectric ceramic composition expressed by a composition formula of $w \cdot Li_2O - x \cdot Na_2O - y \cdot Sm_2O_3 - z \cdot TiO_2$ ($w+x+y+z=100$ mole %) has a high dielectric constant ε, has a low temperature coefficient of resonance frequency τf and has a high Q value. In the sample 67 lacking Li_2O, the absolute value of the temperature coefficient of resonance frequency τf is slightly high.

w, x, y and z are set in the following ranges:

$$0.0 \text{ mole \%} < w \leqq 17.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} \leqq x \leqq 17.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < y \leqq 25.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < z \leqq 80.0 \text{ mole \%}$$

Particularly when w, x, y and z are set in the following ranges, good dielectric properties are obtained:

$$0.0 \text{ mole \%} < w \leqq 15.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} \leqq x \leqq 15.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < y \leqq 20.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < z \leqq 75.0 \text{ mole \%}$$

Description is now made of a fifth embodiment.

A microwave ceramic composition according to the fifth embodiment is obtained by selecting, in a composition formula of $(A^{1+} \cdot A^{1+\prime})_2O - (B^{3+} \cdot B^{3+\prime})_2O_3 - TiO_2$, Li^{1+}, Na^{1+}, Sm^{3+}, and Nd^{3+} as A^{1+}, $A^{1+\prime}$, B^{3+}, and $B^{3+\prime}$, respectively. In the fifth embodiment, high-purity powders of TiO_2, Li_2CO_3, Na_2CO_3, Nd_2O_3, and Sm_2O_3 are used as raw materials, and the mixture ratio of the respective raw materials is changed in the same method as that in the first embodiment, to prepare samples. The dielectric properties of the samples measured in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 7. In the table 7, v, w, x, y and z denote molar fractions, where $v+w+x+y+z=100$ mole %.

TABLE 7

sample number	composition ratio (mole %) $v.Nd_2O_3—w.Li_2O—x.Na_2O—y.Sm_2O_3—z.TiO_2$ v	w	x	y	z	dielectric properties ε	Q value	τ f(PPM/°C.)
97	3.33	4.80	3.33	15.04	73.50	83	750	+24
98	3.33	5.20	3.33	15.60	72.54	81	1250	+3
99	3.33	6.40	3.33	14.72	72.22	79	2250	−71
100	3.33	8.00	3.33	14.40	70.94	77	2200	−99
101	3.33	11.20	3.33	13.76	68.38	67	790	−212
102	3.33	14.40	3.33	13.12	65.82	75	640	−186
103	6.66	3.90	6.66	11.7	71.08	89	1850	−1
104	6.66	3.60	6.66	11.28	71.80	92	1480	+22
105	6.66	4.80	6.66	11.04	70.84	78	2370	−69
106	6.66	6.00	6.66	10.80	69.88	94	1410	−10
107	6.66	8.40	6.66	10.32	67.96	98	860	−10
108	6.66	10.80	6.66	9.84	66.04	113	570	+77

As can be seen from the table 7, a dielectric ceramic composition expressed by a composition formula of $v \cdot Nd_2O_3 - w \cdot Li_2O - x \cdot Na_2O - y \cdot Sm_2O_3 - x \cdot TiO_2$ ($v+w+x+y+z=100$ mole %) has a high dielectric constant ε, has a low temperature coefficient of resonance frequency τf and has a high Q value.

v, w, x, y and z are set in the following ranges:

$$0.0 \text{ mole \%} < v \leqq 25.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} \leqq w \leqq 17.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < x \leqq 17.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < y \leqq 25.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < z \leqq 80.0 \text{ mole \%}$$

Particular when v, w, x, y and z are set in the following ranges, good dielectric properties are obtained:

$$3.0 \text{ mole \%} \leqq v \leqq 7.0 \text{ mole \%}$$
$$3.0 \text{ mole \%} \leqq w \leqq 15.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} \leqq x \leqq 7.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < y \leqq 16.0 \text{ mole \%}$$
$$0.0 \text{ mole \%} < z \leqq 75.0 \text{ mole \%}$$

Description is now made of a sixth embodiment.

A microwave ceramic composition according to the sixth embodiment is obtained by selecting, in a composition formula of $(A^{1+} \cdot A^{1+\prime})_2O - (B^{3+} \cdot B^{3+\prime})_2O_3 - TiO_2$, Li^{1+}, Na^{1+}, Sm^{3+}, and Pr^{3+} as A^{1+}, $A^{1+\prime}$, B^{3+}, and $B^{3+\prime}$, respectively. In the sixth embodiment, high-purity powders of TiO_2, Li_2CO_3, Na_2CO_3, Nd_2O_3, and Pr_6O_{11} are used as raw materials, and the mixture ratio of the respective raw materials is changed in the same method as that in the first embodiment, to prepare samples. The dielectric properties of the samples measured

in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 8. In the table, v, w, x, y and z indicate molar fractions, where v+w+x+y+z=100 mole %.

TABLE 8

sample	composition ratio (mole %) v.Pr_2P_3—w.Li_2O—x.Na_2O—y.Sm_2O_3—z.TiO_2					dielectric properties		
number	v	w	x	y	z	ε	Q value	τ f(PPM/°C.)
109	3.33	4.80	3.33	15.04	73.50	84	830	+26
110	3.33	6.40	3.33	14.72	72.22	81	2050	−50
111	3.33	8.00	3.33	14.40	70.94	78	2000	−97
112	3.33	11.20	3.33	13.76	68.38	69	720	−217
113	3.33	14.40	3.33	13.12	65.82	76	670	−195
114	6.66	3.60	6.66	11.28	71.80	95	1170	+34
115	6.66	4.80	6.66	11.04	70.84	95	1120	+15
116	6.66	6.00	6.66	10.80	69.88	99	1080	+16
117	6.66	8.40	6.66	10.32	67.96	106	560	+20
118	6.66	10.80	6.66	9.84	66.04	115	390	+93

As can be seen from the table 8, a dielectric ceramic composition expressed by a composition formula of v·Pr_2O_3—w·Li_2O—x·Na_2O—y·Sm_2O_3—z·TiO_2 (v+w+x+y+z=100 mole %) has a high dielectric constant ε, has a low temperature coefficient of resonance frequency τf and has a high Q value.

v, w, x, y and z are set in the following ranges:

0.0 mole % < v ≦ 7.0 mole %
0.0 mole % < w ≦ 15.0 mole %
0.0 mole % ≦ x ≦ 7.0 mole %
0.0 mole % < y ≦ 16.0 mole %
0.0 mole % < z ≦ 75.0 mole %

Particularly when v, w, x, y and z are set in the following ranges, good dielectric properties are obtained:

3.0 mole % ≦ v ≦ 7.0 mole %
3.0 mole % ≦ w ≦ 15.0 mole %
3.0 mole % ≦ x ≦ 7.0 mole %
9.0 mole % ≦ y ≦ 16.0 mole %
65.0 mole % ≦ z ≦ 75.0 mole %

Description is now made of a seventh embodiment.

A microwave ceramic composition according to the seventh embodiment is obtained by selecting, in a composition formula of $A^{1+}{}_2O$—CaO—$B^{3+}{}_2O_3$—TiO_2, Li^{1+} and Sm^{3+} as A^{1+} and B^{3+}, respectively. In the seventh embodiment, high-purity powders of TiO_2, Li_2CO_3, $CaCO_3$, and Sm_2O_3 are used as raw materials, and the mixture ratio of the respective raw materials is changed in the same method as that in the first embodiment, to prepare samples. The dielectric properties of the samples measured in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 9. In the table, w, x, y and z denote molar fractions, where v+w+x+y+z=100 mole %.

TABLE 9

sample	composition ratio (mole %) w.Li_2O—x.CaO—y.Sm_2O_3—z.TiO_2				dielectric properties		
number	w	x	y	z	ε	Q value	τ f(PPM/°C.)
119	3.50	20.00	11.28	65.12	90	1840	+164
120	4.80	10.00	15.40	70.16	87	1590	+21
121	4.80	20.00	11.04	64.16	104	1720	+155
122	5.00	10.00	10.00	75.00	89	1390	+55
123	6.00	20.00	10.80	63.20	111	1630	+156
124	6.40	10.00	14.72	68.88	92	1910	+8
125	8.00	10.00	14.40	67.60	95	1780	−8
126	8.40	20.00	10.32	61.28	121	1510	+179
127	11.20	10.00	13.76	65.04	106	1550	+8
128	20.00	10.00	10.00	75.00	75	1700	−44
129	7.00	17.00	13.00	63.00	98	1980	−15
130	8.00	17.00	12.00	63.00	104	1500	+7
131	9.00	16.00	12.00	63.00	105	1550	−2
132	9.00	17.00	11.00	63.00	108	1190	+45
133	12.50	12.50	12.50	62.50	103	1277	+6
134	8.82	23.53	8.82	58.83	123	1156	+154
135	5.56	33.33	5.56	55.55	133	1025	+457
136	2.63	42.11	2.63	52.63	108	1190	+835

As can be seen from the table 9, a dielectric ceramic composition expressed by a composition formula of w·Li_2O—x·CaO—y·Sm_2O_3—z·TiO_2 (w+x+y+z=100 mole %) has a high dielectric constant ε, has a low temperature coefficient of resonance frequency τf and has a high Q value.

Particularly when v, w, x, y and z are set in the following ranges, good dielectric properties are obtained:

0.0 mole % < w ≦ 25.0 mole %
0.0 mole % ≦ x < 50.0 mole %
0.0 mole % < y ≦ 20.0 mole %
0.0 mole % < z ≦ 80.0 mole %

Description is now made of an eighth embodiment.

A microwave ceramic composition according to the eighth embodiment is obtained by selecting, in a composition formula of $A^{1+}{}_2O$—CaO—$B^{3+}{}_2O_3$—TiO_2, Li^{1+} and Nd^{3+} as A^{1+} and B^{3+}, respectively. In the eighth embodiment, high-purity powders of TiO_2, Li_2CO_3, $CaCO_3$, and Nd_2O_3 are used as raw materials, and the

mixture ratio of the respective raw materials is changed in the same method as that in the first embodiment, to prepare samples. The dielectric properties of the samples measured in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method are shown in Table 10. In the table, w, x, y and z indicate molar fractions, where v+w+x+y+z=100 mole %.

TABLE 10

sample number	composition ratio (mole %) $w.Li_2O—x.CaO—y.Nd_2O_3—z.TiO_2$ w	x	y	z	dielectric properties ϵ	Q value	τ f(PPM/°C.)
137	14.52	6.45	14.52	64.52	104	810	−129
138	4.00	16.66	12.53	66.80	109	672	+8
139	5.00	16.66	12.27	65.73	114	790	+5
140	6.70	16.66	12.00	64.67	118	802	+3
141	9.30	16.66	11.47	62.53	118	820	+12
142	12.00	16.66	10.93	60.40	124	662	+18
143	18.00	16.66	8.74	56.60	141	405	+25
144	8.50	30.50	5.50	55.50	151	1785	+275
145	1.70	28.57	8.23	61.49	109	1265	+185
146	2.14	28.57	8.57	60.71	110	1500	+157
147	3.43	28.57	7.89	60.11	124	834	+128
148	6.00	28.57	7.37	58.06	129	1105	+131
149	12.50	12.50	12.50	62.50	125	879	+38
150	8.82	23.53	8.82	58.83	135	989	+171
151	5.56	33.33	5.56	55.55	141	962	+323
152	2.63	42.11	2.63	52.63	150	1683	+472

As can be seen from the table 10, a dielectric ceramic composition expressed by a composition formula of $w{\cdot}Li_2O-x{\cdot}CaO-y{\cdot}Nd_2O_3-z{\cdot}TiO_2$ (w+x+y+=100 mole %) has a high dielectric constant ϵ, has a low temperature coefficient of resonance frequency τf and has a high Q value.

w, x, y and z set in the following ranges:

$$0.0 \text{ mole } \% < w \leqq 25.0 \text{ mole } \%$$
$$0.0 \text{ mole } \% \leqq x < 50.0 \text{ mole } \%$$
$$0.0 \text{ mole } \% < y \leqq 20.0 \text{ mole } \%$$
$$0.0 \text{ mole } \% < z \leqq 80.0 \text{ mole } \%$$

Particularly when w, x, y and z are set in the following ranges, good dielectric properties are obtained;

$$0.0 \text{ mole } \% < w \leqq 20.0 \text{ mole } \%$$
$$0.0 \text{ mole } \% \leqq x < 50.0 \text{ mole } \%$$
$$0.0 \text{ mole } \% < y \leqq 20.0 \text{ mole } \%$$
$$50.0 \text{ mole } \% \leqq z \leqq 80.0 \text{ mole } \%$$

Description is now made of a ninth embodiment. A ceramic composition according to the ninth embodiment is obtained by mixing the ceramic composition $(Li_{1/2}{\cdot}B^{3+}{}_{1/2})$ TiO_3 obtained in the above described first embodiment and a ceramic composition $(Na_{1/2}{\cdot}C^{3+}{}_{1/2})TiO_3$ having dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the plus side. At this time, Nd^{3+} or Sm^{3+} and Nd^{3+} or Sm^{3+} are respectively selected as B^{3+} and C^{3+}.

Samples are prepared in the same method as that in the first embodiment, and the dielectric constant ϵ, the Q value, and the temperature coefficient of resonance frequency τf of the samples are measured in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method.

The results of the measurements are shown in Table 11 and Table 12. In the tables, a, b, c and d are as follows:

a: $(Li_{1/2}.Nd_{1/2})$ TiO_3	b: $(Na_{1/2}.Nd_{1/2})$ TiO_3
c: $(Li_{1/2}.Sm_{1/2})$ TiO_3	d: $(Na_{1/2}.Sm_{1/2})$ TiO_3

TABLE 11

sample number	mixture ratio (mole %)		dielectric properties dielectric constant ϵ	Q value	τ f (PPM/°C.)
	a	b			
153	80	20	100	851	−15
154	60	40	108	511	58
155	40	60	106	513	205
156	20	80	88	881	245
	a	d			
157	80	20	95	1099	−7
158	60	40	99	914	32
159	40	60	95	1072	144
160	20	80	75	1566	185

TABLE 12

sample number	mixture ratio (mole %)		dielectric properties dielectric constant ϵ	Q value	τ f (PPM/°C.)
	c	b			
161	80	20	76	1665	−64
162	60	40	89	1297	12
163	40	60	99	910	162
164	20	80	90	1081	220
	c	d			
165	80	20	70	1884	−69
166	60	40	79	2023	17
167	40	60	81	1314	116
168	20	80	68	1537	178

As can be seen from the tables 11 and 12, a ceramic composition having a high dielectric constant ϵ, having a low temperature coefficient of resonance frequency τf and having a high Q value is obtained by mixing a ceramic composition $(Na_{1/2}{\cdot}C^{3+}{}_{1/2})$ TiO_3 (C^{3+}: Nd^{3+}, Sm^{3+}) having a high dielectric-constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the plus side and a ceramic composition $(Li_{1/2}{\cdot}B^{3+}{}_{1/2})$ TiO_3 (B^{3+}: Nd^{3+}, Sm^{3+}) having a high dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the minus side.

FIG. 1 is a characteristic diagram showing the characteristic curve of a dielectric constant ϵ and a temperature coefficient of resonance frequency τf against the

mixture ratio of $(Li_{1/2}\cdot Sm_{1/2})$ TiO_3 to $(Na_{1/2}\cdot Sm_{1/2})$ TiO_3. The mixture ratio is thus changed, to obtain ceramic compositions having various properties.

The ceramic composition according to the ninth embodiment shown in the tables 11 and 12 is obtained by mixing the ceramic composition $(Li_{1/2}\cdot Nd_{1/2})$ TiO_3 or $(Li_{1/2}\cdot Sm_{1/2})$ TiO_3 obtained in the above described first embodiment and a ceramic composition $(Na_{1/2}\cdot Nd_{1/2})$ TiO_3 or $(Na_{1/2}\cdot Sm_{1/2})$ TiO_3 having a high dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the plus side. When the same ceramic composition as that in the ninth embodiment is obtained using high-purity powders of TiO_2, Li_2CO_3, Na_2CO_3, Sm_2O_3, and Nd_2O_3 as raw materials, the mixture ratios of the respective raw materials are as shown in Table 13 to Table 15. The dielectric properties of samples of the ceramic composition formed in the mixture ratios are the same as those of the samples shown in the tables 11 and 12. In the tables 13 to 15, sample numbers in parentheses correspond to the samples shown in the tables 11 and 12.

TABLE 13

sample number	composition ratio (mole %) $w.Li_2O—x.Na_2O—y.Nd_2O_3—z.TiO_2$ w	x	y	z
169(153)	13.33	3.33	16.67	66.67
170(154)	9.99	6.77	16.67	66.67
171(155)	6.77	9.99	16.67	66.67
172(156)	3.33	13.33	16.67	66.67

TABLE 14

sample number	composition ratio (mole %) $v.Nd_2O_3—w.Li_2O—x.Na_2O—y.Sm_2O_3—z.TiO_2$ v	w	x	y	z
173(157)	13.34	13.33	3.33	3.33	66.67
174(158)	9.99	9.99	6.67	6.68	66.67
175(159)	6.68	6.67	9.99	9.99	66.67
176(160)	3.34	3.33	13.33	13.33	66.67
177(161)	3.33	13.33	3.33	13.34	66.67
178(162)	6.68	9.99	6.67	9.99	66.67
179(163)	9.99	6.67	9.99	6.68	66.67
180(164)	13.33	3.33	13.33	3.34	66.67

TABLE 15

sample number	composition ratio (mole %) $w.Li_2O—x.Na_2O—y.Sm_2O_3—z.TiO_2$ w	x	y	z
181(165)	13.33	3.33	16.67	66.67
182(166)	9.99	6.67	16.67	66.67
183(167)	6.67	9.99	16.67	66.67
184(168)	3.33	13.33	16.67	66.67

Description is now made of a tenth embodiment using $CaTiO_3$ as a ceramic composition having a high dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the plus side.

Table 16 shows the results of measurements made of the dielectric properties of samples of a dielectric composition obtained by selecting, in a composition formula of $(Li_{1/2}\cdot B^{3+}{}_{1/2})$ TiO_3—$CaTiO_3$, Nd^{3+} or Sm^{3+} as B^{3+} in the same manner as that in the first embodiment in the neighborhood of the measurement frequency of 3 GHz using the Hakki-Coleman method.

In the table 16, a and c are the same as those in the tables 11 and 12.

TABLE 16

sample number	mixture ratio (mole %)	$CaTiO_3$	dielectric properties: dielectric constant ϵ	Q value	τf (PPM/°C.)
	a				
185	80	20	125	879	38
186	60	40	135	989	171
187	40	60	141	962	323
188	20	80	150	1683	472
	c				
189	80	20	103	1277	6
191	60	40	123	1156	154
192	40	60	133	1025	305
193	20	80	144	1822	457

As can be seen from the table 16, a dielectric ceramic composition having a dielectric constant ϵ which takes a large value exceeding 100, having a low temperature coefficient of resonance frequency τf and having a high value is obtained.

A characteristic curve of a dielectric constant ϵ and a temperature coefficient of resonance frequency τf against the mixture ratio of $(Li_{1/2}\cdot B^{3+}{}_{1/2})$ TiO_3 to $CaTiO_3$ is shown in FIG. 2 ($B^{3+}=Nd^{3+}$) and FIG. 3 ($B^{3+}=Sm^{3+}$).

Description is now made of the tenth embodiment using $CaTiO_3$ as a ceramic composition having a high dielectric constant ϵ and having a temperature coefficient of resonance frequency τf which is large on the plus side.

The ceramic composition according to the tenth embodiment shown in the table 16 is obtained by mixing the ceramic composition $(Li_{1/2}\cdot Nd_{1/2})$ TiO_3 or $(Li_{1/2}\cdot Sm_{1/2})$ TiO_3 obtained in the above described first embodiment and $CaTiO_3$. When the same ceramic composition as that in the tenth embodiment is obtained using high-purity powders of TiO_2, Li_2CO_3, Sm_2O_3, Nd_2O_3, and $CaCO_3$ as raw materials, the mixture ratios of the ceramic composition are as shown in Table 17 and Table 18. The dielectric properties of samples of a ceramic composition formed in the mixture ratios are the same as those of the samples shown in the table 16. In the tables 17 and 18, sample numbers in parentheses correspond to the samples shown in the table 16.

TABLE 17

sample number	composition ratio (mole %) $w.Li_2O—x.CaO—y.Nd_2O_3—z.TiO_2$ w	x	y	z
194(185)	12.50	12.50	12.50	62.50
195(186)	8.82	23.53	8.82	58.83
196(187)	5.56	33.33	5.56	55.55
197(188)	2.63	42.11	2.63	52.63

TABLE 18

sample number	composition ratio (mole %) $w.Li_2O—x.CaO—y.Sm_2O_3—z.TiO_2$ w	x	y	z
199(189)	12.50	12.50	12.50	62.50
199(190)	8.82	23.53	8.82	58.83
200(191)	5.56	33.33	5.56	55.55
201(192)	2.63	42.11	2.63	52.63

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope

of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A microwave dielectric ceramic composition comprising a composition according to the formula $(A^{1+}{}_{\frac{1}{2}} \cdot B^{3+}{}_{\frac{1}{2}})TiO_3$, wherein A^{1+} is Li^{1+}, and B^{3+} is a member of the group consisting of Nd^{+}, Sm^{3+}, Co^{3+} and Pr^{3+}.

2. A microwave dielectric ceramic composition consisting essentially of: 100 parts by weight of a ceramic $(Li_{\frac{1}{2}} \cdot Nd_{\frac{1}{2}})TiO_3$; and 10 parts by weight of a member from the group consisting of MgO, CoO, and ZnO.

3. A microwave dielectric ceramic composition consisting essentially of: 100 parts by weight of a ceramic $(Li_{\frac{1}{2}} \cdot Pr_{\frac{1}{2}})TiO_3$; and 10 parts by weight of a member from the group consisting of MgO, CoO, and ZnO.

4. A microwave dielectric ceramic composition consisting essentially of: 100 parts by weight of a ceramic $(Li_{\frac{1}{2}} \cdot Sm_{\frac{1}{2}})TiO_3$; and 10 parts by weight of a member from the group consisting of $CaCO_3$, $SrCO_3$, and ZnO.

5. A microwave dielectric ceramic composition comprising a composition according to the formula $w \cdot A^{1+}{}_2O - x \cdot A^{1+\prime}{}_2O - y \cdot B^{3+}{}_2O_3 - z \cdot TiO_2$, wherein $w+x+y+z=100$ % mole, A^{1+} is Li^{1+}, $A^{1+\prime}$, is Na^{1+}, and B^{3+} is a member of the group consisting of Nd^{3+} or Sm^{3+}.

6. The microwave dielectric ceramic composition according to claim 2, wherein B^{3+} is Nd^{3+}, and w, x, y and z are in the following ranges:

0.0 mole $< w \leqq 17.0$ mole %,
0.0 mole $\leqq x \leqq 17.0$ mole %,
0.0 mole $< y \leqq 25.0$ mole %,
0.0 mole $< z \leqq 80.0$ mole %.

7. The microwave dielectric ceramic composition according to claim 2, wherein B^{3+} is Sm^{+}, and w, x, y and z are in the following ranges:

0.0 mole $< w \leqq 17.0$ mole %,
0.0 mole $\leqq x \leqq 17.0$ mole %,
0.0 mole $< y \leqq 20.0$ mole %,
0.0 mole $< z \leqq 75.0$ mole %.

8. A microwave dielectric ceramic composition comprising a composition according to the formula $v \cdot B^{3+\prime}{}_2O_3 - w \cdot A^{1+}{}_2O - x \cdot A^{1+\prime}{}_2O - y \cdot B^{3+}{}_2O_3 - z \cdot TiO_2$, wherein, A^{1+} is Li^{1+}, $A^{1+\prime}$ is Na^{1+}, B^{3+} is Sm^{3+}, and $B^{3+\prime}$ is a member of the group consisting of Nd^{3+} and Pr^{3+}.

9. The microwave dielectric ceramic composition according to claim 5, wherein $B^{3+\prime}$ is Nd^{+} and v, w, x, y and z are in the following ranges:

0.0 mole $< v \leqq 25.0$ mole %,
0.0 mole $< w \leqq 17.0$ mole %,
0.0 mole $\leqq x \leqq 17.0$ mole %,
0.0 mole $< y \leqq 25.0$ mole %,
0.0 mole $< z \leqq 80.0$ mole %.

10. The microwave dielectric ceramic composition according to claim 5, wherein $B^{3+\prime}$ is Pr^{3+}, and v, w, x y and z are in the following ranges:

0.0 mole $< v \leqq 7.0$ mole %,
0.0 mole $< w \leqq 15.0$ mole %,
0.0 mole $\leqq x \leqq 7.0$ mole %,
0.0 mole $< y \leqq 16.0$ mole %,
0.0 mole $< z \leqq 75.0$ mole %.

11. A microwave dielectric ceramic composition comprising a composition according to the formula $w \cdot A^{1+}{}_2O - x \cdot CaO - y \cdot B^{3+}O_3 - z \cdot TiO_2$, wherein $w+x+y+z=100$ % mole, A^{1+} is Li^{1+}, and B^{3+} is a member of the group consisting of Sm^{3+} an Nd^{3+}.

12. The microwave dielectric ceramic composition according to claim 8, wherein B^{3+} is Sm^{3+}, and w, x, y and z are in the following ranges:

13. The microwave dielectric ceramic composition according to claim 8, wherein B^{3+} is Nd^{3+}, and w, x, y and z are in the following ranges:

0.0 mole $< w \leqq 25.0$ mole %,
0.0 mole $\leqq x < 50.0$ mole %,
0.0 mole $< y \leqq 20.0$ mole %,
0.0 mole $< z \leqq 80.0$ mole %.

0.0 mole $< w \leqq 25.0$ mole %,
0.0 mole $\leqq x < 50.0$ mole %,
0.0 mole $< y \leqq 20.0$ mole %,
0.0 mole $< z \leqq 80.0$ mole %.

14. A microwave dielectric ceramic composition comprising a composition according to the formula $x \cdot (Li_{\frac{1}{2}} \cdot B^{3+}{}_{\frac{1}{2}})\ TiO_3 - (100-x)\ (Na_{\frac{1}{2}} \cdot C^{3+}{}_{\frac{1}{2}})\ TiO_3$, wherein 0 mole $\% < x < 100$ mole %, and B^{+} and C^{3+} are, respectively, a member of the group consisting of Nd^{3+} and Sm^{3+}.

15. A microwave dielectric ceramic composition comprising a composition according to the formula $x \cdot (Li_{\frac{1}{2}} \cdot B^{3+}{}_{\frac{1}{2}})\ TiO_3 - (100-x)\ (CaTiO_3$, wherein 0 mole $\% < x < 100$ mole %, and B^{3+} is a member of the group consisting of Nd^{3+} and Sm^{3+}.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,188,993 Page 1 of 2

DATED : February 23, 1993

INVENTOR(S) : Hisakazu Takashi et al

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 8, TABLE 6, change "w.Li_2O-x.Na_2O-y.Nd_2O_3-z.TiO_2" to --w.Li_2O-x.Na_2O-y.Sm_2O_3-z.TiO_2--.

Column 9, TABLE 6, change "w.Li_2O-x.Na_2O-y.Nd_2O_3-z.TiO_2" to --w.Li_2O-x.Na_2O-y.Sm_2O_3-z.TiO_2--.

Column 11, TABLE 8, change "v.Pr_2P_3-w.Li_2O-x.Na_2O-y.Sm_2O_3-z.TiO_2" to --v.Pr_2O_3-w.Li_2O-x.Na_2O-y.Sm_2O_3-z.TiO_2--.

Column 17, line 2,, change "according to claim 2," to --according to claim 5,--.

Column 17, line 2, change "according to claim 2," to --according to claim 5,--.

Column 18, line 2,change "according to claim 5," to --according to claim 8,--.

Column 18 line 2, change "according to claim 5," to --according to claim 8.--.

Column 18, line 2, change "according to claim 8," to --according to claim 11,--.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,188,993

DATED : February 23, 1993

INVENTOR(S) : Hisakazu Takashi et al

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 18, line 2, change "according to claim 8, "to --according to claim 11, --.

Signed and Sealed this

Fourteenth Day of June, 1994

Attest:

Bruce Lehman

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks